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Current global challenges to the use of fumigants

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ABSTRACT

The two most important limitations of phosphine fumigation are: (a) long exposure times; and (b) the danger of developing resistant insect populations. It is evident that insect resistance is a serious concern that threatens the continued effective use of phosphine. Phosphine fumigation protocols have been revised in different countries to tackle the problem of insect resistance to the fumigant. In many countries, fumigation is performed under tarpaulins or a liner with high permeation to the fumigant, with permeable floors where retention of the fumigant is not measured. This requires repeat fumigations that most probable increases resistance levels and selects for insects with a higher phosphine tolerance. To deal with the question 'what degree of gastightness is needed for a successful fumigation' some comparative assessments were made to provide practical guidelines. In this paper other registered fumigants are reviewed, they suffer from the limitation that they may be useful for application using special equipment or under specific conditions. Sulfuryl fluoride (SF) has not been registered as widely as phosphine. The SF has potential applications in disinfesting flour mills and food factories. It can be used effectively for insect pest control in dry tree nuts and food grain, but data are scarce on the effect of SF on quality of the treated commodity and persistence of residues. Propylene oxide (PPO) has the property to act within very short exposure times on storage insects. It is a safe fumigant for use on food, and is registered and used in the USA as a sterilant for commodities such as dry and shelled walnuts (*Juglans regia* L.), spices, cocoa (*Theobroma cacao* L.) powder and nutmeats. The PPO should be applied under low pressure or in CO_2-enriched atmospheres. Ethyl formate (EF) has been tested against insect pests of food commodities. It is rapidly toxic to storage insects including psocids. The EF should be used in mixture with CO_2.

Key words: Ethyl formate, Gastightness, Phosphine, Propylene oxide, Sulfuryl fluoride

Of the 16 fumigants listed in common use some 32 years ago by Bond (1984), only very few remain today. Most of these fumigants have been withdrawn or discontinued on the grounds of environmental safety, cost, carcinogenicity and other factors. Methyl bromide (MB) has been phased out by 2015, because of its contribution to stratospheric ozone depletion (UNEP, 2002). In cases where there is a value for MB fumigation, exemptions for quarantine and pre-shipment (QPS) purposes, as well as the possibility to apply for exemptions where no alternative exists, the applicant has to demonstrate that every effort is being made to research alternative treatments. In contrast; phosphine remains popular, in many countries, because it is the only remaining registered fumigant.

However, because the long exposures required, many food industries and particularly exporters have been striving for a quick and effective fumigant for insect pest control in food commodities. In addition, the WTO and Free Trade Policies, trade traffic of foodstuffs across the world have been considerably increased to a level that, fumigation for disinfesting stored food commodities has been playing a significant role. Although some developed countries have adopted the approach of zero tolerance of insect pests in food commodities, many insects have developed resistance to phosphine over the last decade (Cao et al., 2003; Savvidou et al., 2003; Daolin et al., 2007). Therefore, the fumigation technology that is required to obtain this zero infestation has been facing constraints because

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of regulatory implementation and the development of resistance of phosphine (Arthur and Rogers, 2003).

The increased demand of competitive markets for quality in food commodities free from pest and pesticide contaminants on the one hand, and the need to find appropriate alternative control measures on the other hand, pose the first challenge. Although efforts have been made to register new fumigants in several countries, and in the development of new technologies as alternative control methods, the limitations that exist in the registration of those newly considered fumigants pose also significant global challenges. The restrictions imposed by regulatory agencies in many countries and particularly in Europe make registration a target very difficult to achieve. The aim of the present paper is to elucidate those new global challenges to the use of gaseous treatments in stored products.

Phosphine

Phosphine is available in solid preparations of aluminum or magnesium phosphide and in cylinders containing carbon dioxide ECO_2 FUME® or nitrogen FRISIN®. Lately, on-site phosphine generators that can release the fumigant up to the rate of 5 kg h^{-1} are available in some countries (Argentina, Chile, China and the USA). Metal phosphide formulations with slow or altered rates of phosphine release have been developed and tested in Australia (Waterford and Asher, 2000) and India (Rajendran, 2001).

Gastightness requirement for phosphine fumigation: A major problem in the application of phosphine is the retention of the gas in the fumigated enclosure. Since fumigation in unsealed silos does not kill pests at all stages. Most of the structures are characterized by lack of gastightness. Only few countries have established standards for gastight silos appropriate for fumigation (Newman, 2006, 2010). Japan has had fumigation gastightness standards since before 1970 (*personal communication:* Jonathan Banks). In most countries fumigation is performed under tarpaulins or a liner with high permeation to the fumigant, with permeable floors where retention of the fumigant is not measured. This requires repeat fumigations that most probable increases resistance levels and selects for insects with a higher phosphine tolerance.

Rajendran et al. (2000) suggested that it is important to maintain a minimum phosphine concentration of 1000 ppm for resistant *Rhyzopertha dominica* and 600 ppm for resistant *Sitophilus oryzae* in a 7 d treatment. Trials show that these levels of gas concentration are not realistic to achieve in silos, so insects will not be controlled at all life stages. The fumigation may appear successful when the adults die but the surviving eggs and pupae will continue to develop and re-infest the grain.

In Australia, a silo is technically considered as sealed if it stands a five-minute half-life pressure test according to the new Australian Standards AS2628 (Standards Australia, 2010). Often silos are constructed as sealed but are not gas-tight, being unsuitable for fumigation.

The question should be what degree of gastightness is needed for a successful fumigation? For this purpose some comparative assessments were made to provide practical guidelines.

In variable pressure test, the structure is pressurized to a value above atmospheric, using a fan. The air supply is then shut off and the pressure is allowed to fall by natural leakage to a new value. The time taken to fall from the high (positive or negative) pressure serves as a measure of the degree of sealing. Time elapse to half the pressure is usually considered for comparisons of gastightness level.

Although these tests are far from being perfect, they provide significant information to the fumigator. If the structure is not gastight any pressure may not be detected. This is an immediate conclusion.

For testing gastightness of stacks under tarpaulin, a very low negative pressure should be exerted; pressure values as low as 50 Pa may be sufficient to estimate the gastightness of the stack.

For testing container gastightness, the pressure exerted may be as high as 250 Pa, if it cannot be pressurized or the pressure drops within 3 s, the container must be checked for leaks, it should be sealed and retested. Pressure decay time should exceed 10 s from 200 to 100 Pa (Graver and Banks, 2008).

For testing metal silos, to minimize the thermal influence tests should be carried out preferably before sunrise and in still weather. A pressure of 250 Pa may be taken as an upper limit, but for some structures even this pressure may cause poor seals to open. Welded steel cells and concrete silos may be able to stand 500 Pa, but higher pressures are usually unnecessary.

Comparative tests with variable pressure tests are scarce. Table 1 was prepared as provisional guidelines based on best estimates available in the literature. The suggested times given in Table 1 were doubled for empty storages as an approximation to the inter-granular airspace, since for barley (*Hordeum vulgare* L.), corn (*Zea mays* L.), rough grain and wheat (*Triticum aestivum* L.), this free space is in the range of 35 to 65% of the total volume.

Banks and Ripp (1984) tested sealed flat storages from 4,500 to 27,000 tonnes capacity and compared the fumigant effectiveness using phosphine with pressure decay time from 150 to 75 Pa. Their tests resulted in successful control of insects when half-life pressure decay was 3 min. for the storage capacity of 15,600 and 16,500 tonnes, whereas full insect control could not be achieved when half-life pressure decay was less than 1 min for capacities of 4,800 tonnes. In Table 1, a minimum of 3 min for large size structures and a minimum of 1.5 min. for the small range served as basis for half-life decay time for full storages.

Development of resistance to phosphine: Phosphine resistance in all major stored grain beetle pests has been documented in many countries like Australia, India, Marocco, Brazil, the USA and China (Collins et al., 2003; Benhalima et al., 2004; Yang, 2006; Pimentel et al., 2009; Opit et al., 2012; Rajendran, 2016). Alice et al. (2014) reported survival of *Cryptolestes* spp. in field trials on rice (*Oryza sativa* L.) stacks under multi-layered cross-laminated sheets with aluminum phosphide applied at the rate of 3 tablets/tonne for 7 d, even when the average gas concentration at the end of the test was 1,047 ppm v/v (range 156–1,151 ppm). Highest level of phosphine resistance has been reported for *Cryptolestes* spp., followed by *R. dominica* and *T. castaneum* in India as in other countries (Rajendran, 2007). Schlipalius et al. (2014) pointed out that it has become apparent that strong resistance to phosphine is increasing in frequency and possibly in the level of resistances found.

From this discussion it is evident that insect resistance is a serious concern that threatens the continued effective use of phosphine. Phosphine fumigation protocols have been revised in different countries to tackle the problem of insect resistance to the fumigant. In these protocols, the only country that has specified the importance of phosphine fumigation only in gastight structures is Australia. It is expected that pest controllers in other countries will adopt similar standards to avoid fumigation in unsealed structures.

Table 1 Provisional recommended ranges for variable pressure test carried out in structures destined for gaseous treatments to control storage insects.

Type of gaseous treatment	Structure volume in cubic meters	Variable pressure test decay time (min.) 250–125 Pa	
		Empty structure	95% full
Fumigants	Up to 500	3	1.5
	500 to 2,000	4	2
	2,000 to 15,000	6	3
MA	Up to 500	6	3
	500 to 2,000	7	4
	2,000 to 15,000	11	6
MA, including airtight storage	Up to 500	10	5
	500 to 2,000	12	6
	2,000 to 15,000	18	9

Source: Nivarro (1998)

Two major restrictions of phosphine are that it requires several days of exposure to achieve the same level of control as that of MB, and that it corrodes copper and its alloys and therefore electrical and electronic items need protection from exposure to the fumigant. Phosphine also reacts to certain metallic salts, which are contained in sensitive items such as photographic film and some inorganic pigments.

NEWLY CONSIDERED FUMIGANTS

Sulfuryl fluoride

Application: Sulfuryl fluoride has been used as a structural fumigant for dry wood termite control for the past 45 years, but it also has potential applications in disinfesting flour mills and food factories (Bell et al., 1999). On 23, January 2004, the US EPA approved the first-time use of sulfuryl fluoride as a fumigant on food which permits the highest levels of inorganic fluoride on food commodities in its history. Derrick et al. (2013) reported that sulfuryl fluoride is currently being examined for use in museums and historic structures as a pest control agent. When Vikane© is properly used little to no visible damage to materials was noted. However, for accepting it as a museum fumigant in-depth analysis of its possible effect on its physical and chemical properties of exposed artifacts would be necessary (Derrick et al., 2013). Sulfuryl fluoride has been registered and used as a structural fumigant in Germany, Sweden and the USA. Sulfuryl fluoride is available under the trade name 'Vikane' containing 99.8% sulfuryl fluoride and 0.2% inert materials. Apart from the USA, China has been producing sulfuryl fluoride (trade name 'Xunmiejin') since 1983 (Guogan et al., 1999). Also, sulfuryl fluoride can be applied under reduced pressure, so that the exposure period can be drastically reduced (Zettler and Arthur, 2000). The fumigant was noted as highly toxic to diapausing larvae of the codling moth, *Cydia pomonella* in stored walnuts (Zettler et al., 1999). Sulfuryl fluoride is also registered under the trade name 'ProFume®' for the protection of stored food commodities (Schneider et al., 2003). ProFume® is registered in the US to allow virtually all mills and food processing facilities to test, adapt and consider adoption as an alternative to MB. Additionally, registration coverage in EC countries for numerous milling and food processing applications is broad, and increasing (TEAP, 2014).

Ovicidal effect: Although it can be used effectively for insect pest control in dry tree nuts and food grain, data are scarce on the effect of SF on quality of the treated commodity and persistence of residues. The fumigant is more penetrative into treated commodities than MB. Insect eggs are the most tolerant stage for sulfuryl fluoride. The relative egg tolerance can be overcome by increasing the exposure period and by raising the treatment temperature (Bell et al., 1999).

Maximum residue limits: The U.S. Environmental Protection Agency has re-evaluated the current science on fluoride and is taking steps to begin a phased-down withdrawal of the pesticide sulfuryl fluoride, a pesticide that breaks down into fluoride and is commonly used in food storage and processing facilities. Although SF residues in food contribute only a very small portion of total exposure to fluoride, when combined with other fluoride exposure pathways, including drinking water and toothpaste, the EPA has concluded that the tolerance (legal residue limits on food) no longer meets the safety standard under the Federal Food, Drug, and Cosmetic Act (FFDCA) and the tolerances for sulfuryl fluoride should be withdrawn (EPA, 2009).

Greenhouse effect: Sulfuryl fluoride has been reported by Mühle et al. (2009), Papadimitriou et al. (2008) and Sulbaek et al. (2009) to be a greenhouse gas which is about 4,000–5,000 times more efficient in trapping infrared radiation (per kg) than carbon dioxide (per kg). Mühle et al. (2009) indicated that annual amounts of sulfuryl fluoride released into the atmosphere (about 2,000 metric tons per year are far lower than the amounts of CO_2 released by hydrocarbon-burning vehicles, industry, and other processes (about 30 billion metric tonnes per year).

Ethyl formate

Ethyl formate (EF) is known as a solvent and is used as a flavouring agent in the food industry. It is naturally present in certain fruits, wine and honey. In India, extensive laboratory tests against insect pests of food commodities and field trials on bagged cereals, spices, pulses, dry fruits and oilcakes have been carried out on the fumigant (Muthu et al., 1984). Ryan and Bishop (2003) reported on non-flammable EF/liquid carbon dioxide fumigant mixture. Ethyl formate, as Eranol, has long been used for the protection of dried fruits in Australia. It has been found suitable for in-package treatment of dried fruits. Studies in Australia indicate that, unlike phosphine, EF is rapidly toxic to storage insects including psocids (Annis and Graver, 2000).

Application: Ren and Mahon (2003) carried out field trials on EF for fumigation of on-farm storage in bulk of wheat (125 tonnes), sorghum [*Sorghum bicolor* (L.)] (140 tonnes) and faba beans (*Vicia faba* L.) split (75 tonnes). The liquid EF was applied as a pulsed, or double, dose to the top of the grain through a polyvinyl chloride probe. In each pulse, 85 g/tonne was applied, total dosage 170 g/tonne. After 2–4 h of the first pulse, the second pulse was applied. To maintain EF concentrations below the flammable level, reduce vapourization, maintain an effective concentration of ethyl formate for > 20 h, and to avoid liquid ethyl formate accumulating at the bottom of the bin, this method of application was chosen. Those field trials reported by Ren and Mahon (2003) have shown that EF has good potential as a fumigant in unsealed farm bins. To encourage applying EF in un-sealed bins may be questionable from the aspect of leading to future resistance to the fumigant.

A significant point to consider during the application of EF is that the application technology as in combination with carbon dioxide or the fumigant alone has different dosages. Experiments carried out by Rajendran (2009) on 160 tonnes wheat stacks at 27°C showed that a dose of 214 gm^{-3} for 72 h was adequate. While Damcevski et al. (2010) report on the successful application of the formulation of Vapormate^{TM} to achieve complete control of *R. dominica* and *T. castaneum* with 63 and 76 gm^{-3} EF, respectively, with exposure for 24 h.

In practice to purge through a tube using EF in a mixture with carbon dioxide, a vapourizer is needed. This is a heated coil through which the fumigant mixture is conveyed into the fumigation chamber. In treating large volumes of commodity, even a 20 ft (6.1 m) container size, the aspect of application EF either directly as Ren and Mahon (2003) into the grain mass or through an appropriate evaporator needs to be elaborated. Tarr et al. (2004) carried out two fumigations with EF in shipping containers. The first used liquid EF treated with 60 g m^{-3} of EF vapour for 44 h and demonstrated that this fumigant worked in cold conditions. The second demonstration used CO_2 as a carrier gas, thereby reducing flammability and improving distribution of EF. These aspects of practical application are lacking in the literature.

Ryan and deLima (2013) reported that EF applications have been limited because of high treatment costs with cereal grains and phytotoxic issues with fresh produce.

Maximum residue limits: For the registration of a fumigant in a country the established maximum residue limits (MRL) is an important aspect of the process.

Ethyl formate has a long list of products for which the MRLs were established (Default MRL of 0.01 mg kg^{-1}according to Art 18(1)(b) Reg 396/2005. EC pesticide data base 2005). In Australia, EF is permitted for use but no MRL level required since it also occurs at natural levels in barley, wheat, cereals and pulses (Outturn Standards 2013/14, 2013). Australia has been using EF on dried fruits final package. In general, it is considered as an active constituent excluded from the requirements of APVMA approval (APVMA, 2016).

Propylene oxide

Propylene oxide (PPO) is a colourless and flammable liquid, and is used as a food emulsifier, surfactant, cosmetics and starch modifier. Under normal temperature and pressure PPO has a relatively low boiling point (35°C) and a noticeable ether odor (Weast et al., 1986). It is a safe fumigant for use on food; it is registered and used in the USA as a sterilant for commodities such as dry and shelled walnuts, spices, cocoa powder and nutmeats (Griffith, 1999).

Application: A disadvantage of PPO is that it is flammable at from 3 to 37% in air, and therefore, to avoid flammability it should be applied under low pressure or in CO_2 enriched atmospheres. Griffith (1999), in preliminary tests on some stored-product pests, indicated that PPO has insecticidal properties under vacuum conditions as a fumigant. Navarro et al. (2004) studied the relative effectiveness of PPO alone, and in combination with low pressure or CO_2. The great advantage of PPO is its extremely fast action on insects. Very short exposure times are required to control all stages of storage insects (Isikber et al., 2004). To purge PPO through a tube in a mixture with carbon dioxide, a vapourizer is needed.

Maximum residue limits: The PPO has a limited list of maximum residue limits (MRLs) that make difficult its registration in countries. The current MRL for PPO is for dry and shelled walnuts, spices, cocoa powder and nutmeats is 300 ppm (EPA, 2006). There is currently no specific maximum residue limit (MRL) under the Australia New Zealand Food Standards Code or the New Zealand (Maximum Residue Limit of Agricultural Compounds) Food Standards 2002 (NZ MRL Standard) for the presence of PPO residues. The maximum levels of PPO detected (1.3 mg/kg) were less than 0.5% of the present USA tolerance, specified in Part 180, Title 40 of the Code of Federal Regulation (300 mg/kg in pistachios). The NZ MRL Standard does have a default MRL of 0.1 mg $kg^{-1}$for residues of agricultural compounds not specified in the Standard. Eight samples of pistachios (*Pistacia vera* L.) contained PPO residues at concentrations greater than 0.1 mg kg^{-1} (Wilson et al., 2013).

CONCLUSION

No fumigant that has a broad spectrum of action like MB, and is inexpensive like phosphine, is presently available. Although there is no doubt that fumigation technology is extremely important for the protection of stored products, many demands are required from potential alternative fumigants, from the sensitivity and lack of resistance of target pests to requirements for registration of new fumigants and re-registration to maintain the use of old fumigants. However, there is increasing public concern over the adverse effects of pesticide residues in food and the environment. Existing gaseous alternatives to MB and phosphine suffer from the limitation that they may be useful for treating a particular type of commodity or for application in a specific situation only. Sulfuryl fluoride seems to emerge as a promising candidate fumigant for disinfesting stored food commodities, food-processing facilities and as a quarantine fumigant. Other fumigants are suitable to specific uses, such as propylene oxide for dry and shelled walnuts, spices, cocoa powder and nutmeats, ethyl formate can be suitable for dried fruits, cereals and grains. The global challenges in stored products are the development of new and safer gaseous treatments, and new application methods that are commercially feasible.

REFERENCES

Alice JR, Kavitha-Abirami PS, Alagusundaram K, Chakraborty CV, Chadda IC (2014) Study on effective fumigation in Indian warehouses. In: Arthur FH, Kengkanpanich R, Chayaprasert W, Suthisut D (Eds) Proceedings 11th Int. Work. Conf. on Stored Product Protection, 24–28 November 2014, Chiang Mai, Thailand, pp 480–487.

Annis PC, Graver JE van S (2000) Ethyl formate – a fumigant with potential for rapid action. In: 2000 Annual International Research Conference on Methyl Bromide Alternatives and Emissions Reductions, Orlando, 6–9 November, 2000, pp 70–1; 70–3.

APVMA (2016) http://apvma.gov.au/node/4176#e Accessed 30 May, 2016.

Arthur FH, Rogers T (2003) Legislative and regulatory actions affecting insect pest management for postharvest systems in the United States. In: Credland PF, Armitage DM, Bell CH, Cogan PM, Highley E (Eds) Advances in Stored Product Protection. Proceedings of the 8th International Working Conference on Stored-product Protection, York, CAB International, Oxon, UK, pp 435–438.

Banks HJ, Ripp BE (1984) Sealing of grain storages for use with fumigants and controlled atmospheres. In: Proc 3rd Int Work Conf on Stored-Product Entomology. Kansas State University, Manhattan, pp 375–390.

Bell CH, Savvidou N, Smith TJW (1999) The toxicity of sulfuryl fluoride (Vikane) to eggs of insect pests of flourmills. In: Zuxun J, Quan L, Yongsheng L, Xianchang T, Lianghua G (eds) Proceedings of the Seventh International Working Congerence on Stored Product Protection, October 1998, Beijing, China, Sichuan Publishing House of Science and Technology, Chengdu, pp 345–350.

Benhalima H, Chaudhry M Q, Mills KA, Price NR (2004) Phosphine resistance in stored-product insects collected from various grain storage facilities in Morocco. Jounal of Stored Products Research **40**(3): 241–249.

Cao Y (2006) Survey of the resistance of stored-grain pests to phosphine in China. Journal of Henan University of Technology (Natural Science Edition). http://en.cnki.com.cn/Article_en/CJFDTOTAL-ZZLS200601000.htm Accessed 14 June 2016.

Cao Y, Song Y, Sun G (2003) A survey of psocid species infesting stored grain in China and resistance to phosphine in field populations of *Liposcelis entomophila*. In: Credland PF, Armitage DM, Bell CH, Cogan PM, Highley E (Eds). Advances in Stored Product Protection. Proceedings of the 8th International Working Conference on Stored-product Protection, York, CAB International, Oxon, UK, pp 662–667.

Collins PJ, Emery RN, Wallbank BE, Credland PF, Armitage DM, Bell CH, Highley E (2003) Two decades of monitoring and managing phosphine resistance in Australia. In: Advances in Stored Product Protection. In: Proceeding 8rd Int. Work Conf on Stored Product Protection, York, UK, 22–26 July 2002, pp 570–575, CABI Publishing, Wallingford, England.

Damcevski KA, Dojchinov G, Woodman JD, Haritos VS (2010) Efficacy of vaporised ethyl formate/carbon dioxide formulation against stored-grain insects: effect of fumigant concentration, exposure time and two grain temperatures. Pest Management Science **66**(4): 432–438.

Daolin G, Xiaoping Y, Zhanggui Q, Longde Y, Zili Y, Tianke J (2007) Using carbon dioxide to enhance the efficacy of phosphine fumigation. In: Donahaye EJ, Navarro S, Bell C, Jayas D, Noyes R, Phillips TW (Eds) Proceedings of International Conference on Controlled Atmosphere and Fumigation in Stored Products, 8–13th August 2004, Gold-Coast, Australia. FTIC Ltd. Publishing, Israel. pp 422–428.

Derrick MR, Burgess HD, Baker MT, Binnie NE (2013) Sulfuryl fluoride (Vikane): A review of its use as a fumigant. Journal of American Institute for Conservation 77–90.

EC Pesticide Data Base (2005) http://ec.europa.eu/food/plant/pesticides/eu-pesticides-database/public/? event = active substance.detail & language = EN & selectedID = 2030 Accessed 14 June 2016.

EPA (2006) Reregistration Eligibility Decision (RED) Document for Propylene Oxide List B Case Number 2560. http://nepis.epa.gov/Exe/ZyPDF.cgi/P1007LBZ.PDF?Dockey=P1007LBZ.PDF Accessed 14 June 2016

EPA (2009) EPA Proposes to Withdraw Sulfuryl Fluoride Tolerances. Pesticide Registration Review. USEPA. https://archive.epa.gov/oppsrrd1/registration_review/web/html/evaluations.html Accessed 14 June 2016.

Graver JE van S, Banks HJ (2008) Freight containers are they sufficiently gastight for quarantine and pre-shipment fumigation with methyl bromide in the 21st century. In: Daolin G et al. (Eds) Proceedings of the Eighth International Conference on Controlled Atmospheres and Fumigation in Stored Products, pp 441–445.

Griffith T (1999) Propylene oxide, a registered fumigant, a proven insecticide. In: Obenauf GL, Williams A (Eds) Annual International Research Conference on Methyl Bromide Alternatives and Emissions Reductions, November 1–4 1999, UNEP and USDA, San Diego, California, pp 71.

Guogan X, Zhongmei C, Zhao S, Nengzhi Q (1999) The development of sulfuryl fluoride (SO_2F_2), in China – a brief introduction. In: Zuxun J, Quan L, Yongsheng L, Xianchang T, Lianghua G (Eds). Proceedings of the Seventh International Working Conference on Stored Product Protection, October 1998, Beijing, China. Sichuan Publishing House of Science and Technology, Chengdu, pp 562–566.

Hunt S R (2009) New greenhouse gas discovered: sulfuryl fluoride, 4800x worse than CO_2. TG Daily.

Isikber AA, Navarro S, Finkelman S, Rindner M, Azrieli A, Dias R (2004) Toxicity of propylene oxide at low pressure against life stages of four species of stored product insects. Journal of Economic Entomology **97** (2): 281–285.

Mühle J, Huang J, Weiss RF, Prinn RG, Miller BR, Salameh PK, O'Doherty S (2009) Sulfuryl fluoride in the global atmosphere. Journal of Geophysical Research: Atomospheres 14(D5):

Muthu M, Rajendran S, Krishnamurthy TS, Narasimhan KS, Rangaswamy JR, Jayaram M, Majumder SK (1984) Ethyl formate as a safe general fumigant. In: Proceeding of International concerence Controlled Atmosphere and Fumigation in Grain Storages, 11–22 April, 1983, Perth, Australia, pp 369–393.

Navarro S (1999) Pressure tests for gaseous applications in sealed storages: Theory and practice. In: Zuxun J, Quan L, Yongsheng L, Xianchang T, Lianghua G (Eds). Proceedings of the Seventh Working Conference on Stored Product Protection, Sichuan Publishing House of Science and Technology, Chengdu, Sichuan Province, Peoples Republic of China, vol 1, pp 385–390.

Navarro S, Isikber AA, Finkelman S, Rindner M, Azrieli A, Dias R (2004) Effectiveness of short exposures of propylene oxide alone and in combination with low pressure or carbon dioxide against *Tribolium castaneum*

(Herbst) (Coleoptera: Tenebrionidae). Journal of Stored Products Research **40**: 197–205.

Newman CR (2006) Application of sealing technology to permanent grain storage in Australia. In: Lorini I, Bacaltchuk B, Beckel H, Deckers D, Sundfeld E, Bortolini L (Eds) Proceedings of the Ninth Conference on Stored-Product Protection, 15–18 October 2006, Brazilian Post-Harvest Association, Passo Fundo, RS, Brazil, pp 1,305–1,315.

Newman CR (2010) A novel approach to limit the development of phosphine resistance in Western Australia. Julius-Kühn-Archiv (425), 1038.

Opit GP, Phillips TW, Aikins MJ, Hasan MM (2012) Phosphine resistance in *Tribolium castaneum* and *Rhyzopertha dominica* from stored wheat in Oklahoma. Journal of Economic Entomology **105**(4): 1,107–1,114.

Outturn Standards 2013/14 (2013) Australian Grains Industry Post Harvest Chemical Usage Recommendations and Outturn Tolerances 2013/14, Department of Agriculture. P. 26. http://www.graintrade.org.au/sites/default/files/file/Storage_and_Handling/Outturn%20Tolerances%20V8.pdf Accessed 11 June 2016.

Papadimitriou VC, Portmann RW, Fahey DW, Mühle J, Weiss RF, Burkholder JB (2008) Experimental and theoretical study of the atmospheric chemistry and global warming potential of SO_2F_2. The Journal of Physical Chemistry A **112**(49): 12,657–12,666.

Pimentel MAG, Faroni LDA, Guedes RNC, Sousa AH, Tótola MR (2009) Phosphine resistance in Brazilian populations of *Sitophilus zeamais* Motschulsky (Coleoptera: Curculionidae). Journal of Stored Products Research **45**(1): 71–74.

Protocol M, Deplete OST (2015) 2014 Report of the Methyl Bromide Technical Options Committee 2014 Assessment.

Rajendran S (2001) Alternatives to methyl bromide as fumigants for stored food commodities. Pesticide Outlook, pp 249–252.

Rajendran S (2007) Benchmarking–what makes a good fumigation? In: Donahaye EJ, Navarro S, Bell C, Jayas DS, Noyes R, Phillips TW (Eds) Proceeding of International Conference on Controlled Atmosphere and Fumigation in Stored Products, 8–13th August 2004, Gold- Coast Australia FTIC Ltd. Publishing, Israel, pp 345–365.

Rajendran S (2009) Alternative fumigants for stored grain protection in India. In: Narayanasamy P, Mohan S, Awaknavar JS (Eds) Pest Management in Stored Grains, Chapter 10, Satish Serial Publishing House, Delhi, India, pp 83–91.

Rajendran S (2016) Status of fumigation in stored grains in India. Indian Journal of Entomology **78** (special): 28–38.

Rajendran S, Shrilatha B, Rekha Savanth TL, Nayak KR (2000) Response of field strains of stored grain insect pests to phosphine fumigant. Pesticide Research Journal **12**: 63–67.

Ren Y, Mahon D (2003) Field trials on ethyl formate for fumigation of on-farm storage. In: Wright EJ, Webb MC, Highley E (Eds) Proceedings of the Australian Postharvest Technical Conference, CSIRO Entomology pp 210–216.

Ryan R, Bishop S (2003) VapormateTM: non-flammable ethyl formate/liquid carbon dioxide fumigant mixture. Stored Grain in Australia, pp 190–192.

Ryan RF, Francis de Lima CP (2013) Overview of ethyl formate-85 years as a fumigant. General and Applied Entomology: The Journal of the Entomological Society of New South Wales, 41, 49.

Savvidou N, Mills KA, Pennington A (2003) Phosphine resistance in *Lasioderma serricorne* (F.) (Coleoptera: Anobiidae). In: Credland PF, Armitage DM, Bell CH, Cogan PM, Highley E (Eds) Advances in Stored Product Protection, Proceedings of the 8th International Working Conference on Stored-product Protection, York, CAB International, Oxon, UK, pp 702–712.

Schlipalius DI, Ebert PR, Collins PJ (2014) An emerging international picture of phosphine resistance: opportunities for global cooperation. In: Arthur FH, Kengkanpanich R, Chayaprasert W, Suthisut D (Eds) Proceedings of 11th International Working Conference on Stored Product Protection. 24–28 November 2014, Chiang Mai, Thailand, pp 10–14.

Schneider B, Voglewede C, Houtman B (2003) The technical foundation for precision stored-product-pest fumigation with ProFume™ gas fumigant. In: Credland P F, Armitage DM, Bell CH, Cogan PM, Highley E (Eds) Advances in Stored Product Protection. Proceeding of 8th International Working Conference on Stored-product Protection, York, CAB International, Oxon, UK, pp 561–564.

Standards Australia (2010) AS 2628-2010 Sealed grain-storage silos - Sealing requirements for insect control. http://infostore.saiglobal.com/store/details.aspx?ProductID=1391029. Accessed 11 June 2016.

Sulbaek Andersen MP, Blake DR, Rowland FS, Hurley MD, Wallington TJ (2009) Atmospheric chemistry of sulfuryl fluoride: reaction with OH radicals, Cl atoms and O_3, atmospheric lifetime, IR spectrum, and global warming potential. Environ Sci Technol **43**(4): 1,067–1,070.

Tarr CR, Reuss R, Clingelefer PR, Annis P (2004) Ethyl formate fumigation as a replacement for methyl bromide fumigation in dried vine fruit. Dried Fruit Research and Development Council, Project CSH 64D, CSIRO Plant Industry Horticulture Unit, Stored Grain Research Laboratory CSIRO Entomology. http://www.driedfruitsaustralia.org.au/library/files/o_19q5cdrq11k561jq794b1nmm47u7.pdfAccessed 11 June 2016.

TEAP (2014) Report of the Technology and Economic Assessment Panel, Progress Report, Montreal Protocol on Substances that Deplete the Ozone Layer, United Nations Environment Programme, Ozone Secretariat, October 2014, Nairobi, Kenya: http://ozone.unep.org/Assessment_Panels/TEAP/Reports/TEAP_Reports/MBTOC_CUN_Final_Report_2014_October.pdfAccessed 11 June 2016.

UNEP United Nations Environment Programme (2002)

Montreal Protocol on Substances that Deplete the Ozone Layer, 2002 Assessment, Methyl Bromide Technical Options Committee. Nairobi, Kenya. http://www.unep.org/ozone/teap/Reports/TEAP_Reports/

Waterford CJ, Asher PP (2000) A new formulation of aluminium phosphide providing controlled release of phosphine. In: Obenauf GL, Obenauf R (Eds) Annual International Research Conference on Methyl Bromide Alternatives and Emissions Reductions, Orlando, Florida, pp 77–81.

Weast RC, Astle MJ, Beyer WH (1986) CRC Handbook of Chemistry and Physics, 67^{th} edn, CRC Press, Inc., Boca Raton, Florida.

Wilson M, Lindsay J, Grounds P (2013) Survey of Dried and Edible Nuts, Seeds and Nut and Seed Products Available in New Zealand Prepared for the Ministry for Primary Industries under project MFS/11/05 (MFS/10/14 ctd) – Microbiological – Food Safety, as part of an overall contract for scientific services. July 2013.

Zettler JL, Leesch JG, Gill RF, Tebbets JC (1999) Chemical alternatives for methyl bromide and phosphine treatments for dried fruits and nuts. In: Zuxun J, Quan L, Yongsheng L, Xianchang T, Lianghua G (Eds) Proceedings of the 7th International Working Conference on Stored Product Protection, October 1998, Beijing, China. Sichuan Publishing House of Science and Technology, Chengdu, pp 554–561.

Zettler JL, Arthur FH (2000) Chemical control of stored product insects with fumigants and residual treatments. Crop Protection 19: 577–582.